A novel softener of calico based on biscationic surfactant

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Cationic surfactants derivatives using as softener of calico containing bisquaternary ammonium salt have been synthesized. Epichlorohydrin and N-octadecyldimethylamine have been used to synthesize cationic surfactant 2-hydroxy-1, 3-dis (chlorideoctadecyldimethylammonium) propane (HBOCP). The prepared surfactant is then analyzed using FTIR measurements and 1H-NMR spectra. The critical micelle concentration, foamability and foam stability of HBOCP are determined using standard tools of analysis. The minimum inhibitory concentration of HBOCP to Escherichia coli is found to be 75 ppm, Staphylococcus aureus is immune to bisquaternary ammonium salt cationic surfactant. HBOCP shows better softening property compared to the pristine cotton fabric. The average softness of calico increases from 96 mN to 63 mN after treating by 0.1wt% HBOCP.

Keywords: Bacteriostasis, Bisquaternary ammonium salt, Cationic surfactant, Interfacial properties, Softener

Compared to traditional single quaternary ammonium salt cationic surfactants, bisquaternary ammonium salt possesses advantages, owing to its distinctive features such as excellent surface activity, special phase behavior and better rheology in aqueous solution1-3. The bisquaternary ammonium salt cationic surfactants are effectively being used in the fields of metal anticorrosion4, bactericide5,6, antistatic agent7, and reaction catalyst8,9.

After many years of research, it has been proved that ester quaternary ammonium salt cationic surfactant offers excellent surface activity and better softening effect10. But, in order to obtain a new product with better surface activity and bactericidal performance11,12, the study was aimed at developing bisquaternary ammonium salt cationic surfactant with long-chain alkyl group because this kind of surfactant has two groups of quaternary ammonium salt and lower molecular rigidity. In this study, hyperactive etherifying agent N-octadecylglycidyldimethylammonium chloride (OGDMAC) was firstly synthesized using N-octadecyldimethylamine (OTA) and epichlorohydrin13, and then OGDMAC was allowed to react with N-octadecyldimethylamine hydrochloride (OTAHC), thus producing bisquaternary ammonium salt cationic surfactant 2-hydroxy-1, 3-dis (chlorideoctadecyldimethylammonium) propane (HBOCP).

Experimental Procedure

Reagents and materials

N-octadecyldimethylamine (OTA), epichlorohydrin (EPIC), acetone and ethanol used in this experiment were purchased from Xian-yang Guo-zhong Synthesis and Laundry Ltd., China. All the chemicals were analytical regents and used as received.

The characteristic group in the surfactant produced was tested using a VECTOR-22 Fourier Transform Infrared Spectroscope (Bruker, German). The molecular structure was confirmed using a NMR spectrometer (Bruker, German). JZ-180 interfacial tensiometer (Chengde Tester Ltd., China) was used for the determination of interfacial tension. YX-280 high pressure steam sterilizer (Shang-hai San-shen Medical Device Ltd., China), SW-CJ-1 Cleaning bench (Su-zhou Purification Equipment Ltd., China), and Spx-205B3-Ⅱ Biochemical incubator (Shang-hai Xin-miao Medical Device Ltd., China) were all used to investigate the bactericidal capability.

Synthesis of epoxy active intermediate OGDMAC

0.1 mol N-octadecyldimethylamine (ODA) was added into 0.5 mol epichlorohydrin within 0.5 h, stirred one time per hour at room temperature and then maintained at 35°C for 4 h (ref. 14). The reaction solution was then chilled to -20°C within 3 h and rapidly filtered. The solid product thus obtained was recrystallized twice in acetone. Finally, the newly developed product OGDMAC was kept at room temperature in vacuum desiccator. The mechanism of synthesis was shown in Scheme 1.
Synthesis of HBOCP

0.1 mol OGDMAC was mixed with 0.1 mol octadecyliddimethylamine hydrochloride in 40 mL acetone and stirred at 40°C, for 6 h. Then reaction solution was frozen at -20°C for 3 h. After being filtered, the crude product was recrystallized in the mixture of solvent ethanol and ether (2:1). The purity of HBOCP was checked by TLC using ethylene chloride : methanol : acetic acid (8:2:1), solvent ($R_f = 0.26$). The white solid product was obtained after removing solvent and kept at room temperature in vacuum desiccator.

Surface tension and electrical conductivity

Surface tension measurements were carried out using interfacial tensiometer. The reduction in surface tension ($\gamma$) with respect to surfactant concentration was measured at 25±0.1°C.

The measurements of the conductivity of the surfactant solutions were performed with a conductometer. After investigating the conductivity of the solvent, three successive measurements of the conductivity of the surfactant solutions were carried out at a controlled constant temperature of 25±0.1 °C.

Foamability and foam stability

Foamability and foam stability of HBOCP were studied as per method reported by Shah$^{15}$. A graduated glass cylinder of 100 cm$^3$ volume was used for foam stability and foamability measurements. Surfactant solution (20 cm$^3$) was poured into the calibrated cylinder and given 10 uniform jerks within 10s. The volume of the foam generated was measured as foamability and the time required for the collapse of the foam to half of its initial height was taken as a measure of foam stability. The experiments were repeated at least five times. In this study, octadecyltrimethylammonium chloride (OTAC) and cetyltrimethylammonium chloride (CTAC) were used for comparing the ability of HBOCP.

Bactericidal and antibacterial ability

The new product HBOCP was tested for bactericidal and antibacterial ability in inhibition zone method. The strains were cultivated in nutrient agar liquid at 37°C and maintained at 200 r/min rotational speed in the constant temperature oscillator for 24 h. Then the concentration of bacterial suspension was prepared to 10$^6$/mL after gradient dilution. Filter paper was shaped by 10 mm in diameter, and then immersed in HBOCP aqueous solution with different concentration.

The 0.1 mL bacterial liquid was coated on the sterilized agar plate, and the filter paper immersed in HBOCP aqueous solution was firstly placed on the plate, and then maintained at 37°C for 24 h. In the end, the inhibition zone diameter was used to evaluate the antibacterial activity of HBOCP for Gram positive and Gram negative bacteria.

Employment of HBOCP as a softener of calico

One piece of calico was placed into 0.1wt% HBOCP at 60°C for 30 min (pH 5) and compared to a pristine calico with the same geometric size.

Results and Discussion

The chemical structure of synthetic compound was confirmed by FTIR and $^1$H-NMR. Infrared spectra show peaks at 3414.22, 2919.51, 2850.86, 1468.07, 1097.09, 966.12, 890 and 721.94 cm$^{-1}$. The bands observed at 3414.22 cm$^{-1}$ (stretching vibration peak of -OH) show that the epoxy group is open-looped to form the hydroxyl group. The spectrum also show peaks at 2919.51-2850.86 cm$^{-1}$ (stretching vibration
peak of CH$_3$ and CH$_2$), 1468.06 cm$^{-1}$ (antisymmetric vibration peak of CH$_3$ and CH$_2$), and 1097.09 cm$^{-1}$ (stretching vibration peak of C-N). The bands observed at 966.12 cm$^{-1}$ are related to the special absorption of quaternary ammonium salt. The bands at 721.94 cm$^{-1}$ comes from the stretch vibration absorption of C–H in long chain methylene, and that at 890 cm$^{-1}$ show no characteristics infrared absorption band of epoxy group. This shows that intermediate has reacted completely. The chemical shift of H is in the order by $^1$H-NMR, (CDCl$_3$, 400 MHz) $\delta$=0.88 (t, 3H), 1.30 (q, 6H), 1.86 (s, 1H), 2.63 (s, 12H), 2.86 (d, 4H), 3.05 (m, 1H). So, the structure of synthetic compound is accorded with the structure of HBOCP.

The CMC value of HBOCP was obtained with surface tension and conductivity measurements (Figs 1 and 2). The CMC is found 1.30×10$^{-4}$ mol/L by surface tension measurement (Fig. 1), the surface tension of HBOCP at the CMC being 36.37mN/m. This indicates that HBOCP has good interfacial activity. The CMC value of HBOCP is found to be 1.34×10$^{-4}$ mol/L by conductivity measurement (Fig. 2). The agreement between the CMCs derived from these two methods is satisfactory.

Foamability and foam stability of HBOCP were determined manually as per the method reported by Shah$^{15}$. The foamability of HBOCP is found to be 80 cm$^3$, being 15 cm$^3$ OTAC and 13 cm$^3$ CTAC. The foam stability is 95 min of HBOCP, being 28 min of OTAC and 19 min of CTAC. This indicates that foamability and foam stability of HBOCP perform better than OTAC and CTAC, which attributes to the formation of double long-chain alkyl groups because they are cross-linked by 3C in HBOCP.

All the microbial strains used are of non-invasive species of their genera and thus applicable for analytical work. Escherichia coli and Staphylococcus aureus are common bacteria causing food poisoning. Therefore, we have selected these two bacteria for the screening work. The zone of inhibition is shown in Fig. 3. In the inhibition zone, a lower antibacterial concentration to Escherichia coli and Staphylococcus aureus occurs to HBOCP, whereas it is found that the minimal inhibitory concentration of HBOCP to Escherichia coli is 75 ppm. Such a higher concentration helps to improve its ability, but there is no killing effect of HBOCP to Staphylococcus aureus.

The softerner characterization of HBOCP to calico is given in detail. One piece of calico is placed into 0.1wt% HBOCP at 60 °C for 30 min. Then the longitudinal softness (LS) and transverse softness (TS) are compared to a pristine calico with the same geometric size. The LS and TS of calico with the...
addition of HBOCP are 62 mN and 64 mN respectively, and the average softness (AS) is 63 mN. Relatively, the LS and TS of calico without HBOCP are 97 mN and 95 mN respectively, and the AS is 96 mN. The results reveal that HBOCP has excellent softener performance to calico.

Conclusion
Based on the results of this study, it is inferred that the new product, a long-chain alkyl bisquaternary ammonium salt cationic surfactant of 2-hydroxy-1,3-dis (chloride octadecyl dimethyl ammonium) propane (HBOCP), can be synthesized by N-octadecyldimethylamine and epichlorohydrin. During the synthesis, the CMC of HBOCP is $1.30 \times 10^{-4}$ mol/L, and the surface tension of HBOCP at CMC is 36.37 mN/m. HBOCP possess better foamability and foam stability. In addition, the minimum inhibitory concentration of HBOCP to Escherichia coli rises to 75 ppm and such an intense concentration is helpful to kill Escherichia coli, however, HBOCP is not effective when confronted with Staphylococcus aureus. HBOCP exhibits excellent softener performance when added into calico. In addition, HBOCP gives rise to fantastic attraction of this novel cationic surfactant in dyeing and finishing technology.

References